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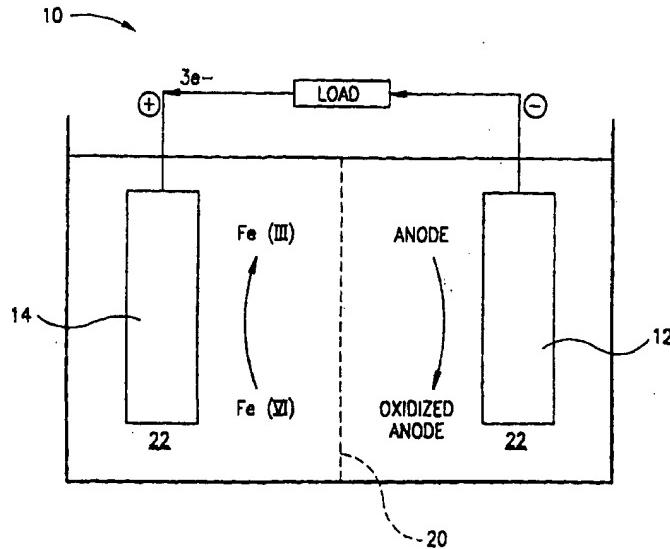
(57) Abstract

An electric storage battery having a solid phase Fe(VI) or Fe(V) or Fe(IV) salt cathode. The anode may be any of a large variety of conventional anode materials capable of being oxidized. The cathode and anode are located in separate half-cells which are in electrochemical contact through an electrically neutral ionic conductor. Optionally means may be provided for impeding the transfer of chemically reactive species between the two half-cells. Also optionally gas separator means may be provided for preventing the build-up of oxygen, hydrogen and other gases.

AN IRON-BASED STORAGE BATTERY

The present invention relates to electric storage batteries. More particularly, the invention relates to a novel electric storage battery with an iron salt as cathode.

5 BACKGROUND OF THE INVENTION

There is an ongoing need for providing novel improved electrical storage batteries, which are low-cost, have a high-energy density and are environmentally acceptable. Among the main types of storage batteries are those in which the cathodes (the positive electrodes) are based on any of
10 PbO_2, HgO, MnO_2 and NiOOH which are known to possess a theoretical capacity in the range of between 224 to 308 Ah/g. However, these cathode materials are considered as hazardous or environmentally unfriendly.

In a very recent U.S. Patent No. 5,429,894, iron-silver (iron in its zero valence state) was suggested as a battery anode (negative). Iron salts in the
15 +2 and +3 valence state, were also suggested as a battery cathode in the past as described, for example, in US 4,675,256 and US 4,795,685.

Prima facie, salts containing iron in the +6 valence state, hereafter called Fe(VI), which are capable of multiple electron reduction, would be capable to provide a higher cathode storage capacity. However,
20 decomposition with reduction of the iron to a less oxidized form (i.e. to a lower valence state) occurs very rapidly, the stability of Fe(VI) salt solutions being only the order of a few hours at room temperature (Anal. Chem. 23, 1312-4, 1951). The Fe (VI) salts may be made by chemical oxidation, such as reported by G. Thompson (J. Amer. Chem. Soc. 73, 1379, 1951), or by
25 precipitation from another Fe(VI) salt, such as reported by J. Gump et al. (Anal. Chem. 26, 1957, 1954). However, as mentioned in a later report by H. Goff et al (J. Amer. Chem. Soc. 93, 6058-6065, 1971), only little is known on the chemistry of Fe(VI) salts. The decomposition of an Fe(VI) salt to a salt in

·2·

which the iron has a lower valence, results in a spontaneous loss of the electrochemical storage capacity. For example, the anion FeO_4^{-2} such as in K_2FeO_4, is unstable in neutral aqueous solutions and decomposes at a rate k_f according to the following equation:

5

$$2FeO_4^{2-} + 3H_2O \rightarrow 2FeOOH + 3/2O_2 + 4OH^-$$
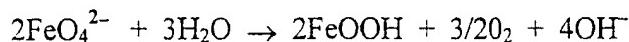
The resultant product in this decomposition, Fe(III)OOH, is environmentally more friendly than any of PbO_2, HgO, MnO_2 and NiOOH,

10 but has a lower electrochemical storage capacity.

It is an object of the present invention to provide a novel type of battery which is inexpensive, highly stable, possesses a high storage capacity, a high voltage and is environmentally friendly.

BRIEF DESCRIPTION OF THE INVENTION:

15 The invention relates to an electrical storage cell, so-called battery, comprising two half-cells which are in electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode in form of a solid-phase Fe(VI) salt in an amount of at least 1% of the half-cell

20 weight, whereby electrical storage is accomplished via electrochemical reduction to a valence of iron salt less than Fe(VI). The high +6 valence state of the iron in said salt provides the advantage of a high storage capacity and high voltage, and iron salts provide an environmental advantage over more toxic materials used for electrochemical electric storage.

25 BRIEF DESCRIPTION OF THE FIGURES:

Figure 1 is a diagrammatic illustration of an Fe(VI) battery according to the invention; and

Figures 2 to 5 illustrate graphically aspects of the performance of various batteries according to the invention as described in the Examples.

DETAILED DESCRIPTION OF THE INVENTION

The novel battery according to the present invention is based on an

5   Fe(VI) (hereafter occasionally referred to as "super iron") half cell serving as cathode, in contact with an anode half cell through an electrically neutral ionic conductor. The discharge in this battery is based on the reduction of the Fe(VI) salt to the +3 valence state. The Fe(VI) salt, e.g. M_2FeO_4 where M is an alkali cation or ammonium, may be prepared by oxidation of iron. Several

10   chemical oxidation methods have been suggested, but among methods which yield Fe(VI) salts of highest purity is the one reported by G. Thompson (J. Amer. Chem. Soc. 73, 1379, 1951). By this method, Fe(VI) salts are obtained through the reaction of a solution of hydroxide and hypochlorite (such as NaOH and NaOCl) with an Fe(III) salt, such as $Fe(NO_3)_3$, as illustrated

15   below:

$$2Fe(OH)_3 + 3ClO^- + 4OH^- \rightarrow 2FeO_4^{-2} + 3Cl^- + 5H_2O \qquad (1)$$
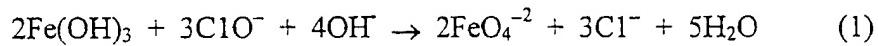
and the resulting Fe(VI) salt (such as K_2FeO_4) is recovered by precipitation from a less soluble solution (such as concentrated KOH), and is then cleaned and dried.

20   Further typical examples of Fe(VI) salts are $M_{x}(FeO_4)_y$ where x and y are integers and M is a cation from the group of alkali earth metal cations, transition metal cations and cations of elements of groups III, IV and V of the periodic table. Examples thereof include, but are not limited to K_2FeO_4, Na_2FeO_4, Li_2FeO_4, Cs_2FeO_4, Rb_2FeO_4, H_2FeO_4, $(NH_4)_2FeO_4$,

25   $(N(C_4H_9)_4)_2FeO_4$, $BeFeO_4$, $MgFeO_4$, $CaFeO_4$, $SrFeO_4$, $BaFeO_4$, Hg_2FeO_4, $HgFeO_4$, Cu_2FeO_4, $CuFeO_4$, $ZnFeO_4$, Ag_2FeO_4, $AsFeO4$, FeO_3, $FeFeO_4$, $Fe_2(FeO_4)_3$, $CrFeO_4$, $MnFeO_4$, $NiFeO_4$, $CoFeO_4$, $Al_2(FeO_4)_3$, $In_2(FeO_4)_3$, $Ga_2(FeO_4)_3$, $SnFeO_4$, $PbFeO_4$, $Sn(FeO_4)_2$, $Pb(FeO_4)_2$.

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Several Fe(VI) syntheses methods which include precipitation from another Fe(VI) salt have been suggested, but the method which yields among the highest purity Fe(VI) salts is the method reported by J. Gump et al. (Anal. Chem. 26, 1957, 1954). By this method, Fe(VI) salts may be obtained
5 through the reaction of an existing Fe(VI) salt (such as K_2FeO_4) with a soluble salt (such $BaCl_2$ or $BaNO_3$) to precipitate another Fe(VI) salt (such as $BaFeO_4$).

Without being bound to any theory, based on the three-electron reduction of these materials as expressed in the equation:

10

$$FeO_4^{2-} + 3H_2O + 3e^- \rightarrow FeOOH + 5OH^- \qquad (2)$$

the electrical storage capacity is high as represented for a few of the materials in Table 1.

15

Table 1

Cathode storage capacity of several Fe(VI) salts

Fe(VI) salt	Formula Wt. G/mole	Charge capacity
Li_2FeO_4	133.8	601 Amp hour/kg
Na_2FeO_4	165.9	485 Amp hour/kg
K_2FeO_4	198.0	406 Amp hour/kg
Cs_2FeO_4	385.6	206 Amp hour/kg
Ag_2FeO_4	335.6	236 Amp hour/kg
$MgFeO_4$	144.1	558 Amp hour/kg
$CaFeO_4$	159.9	505 Amp hour/kg
$SrFeO_4$	207.5	387 Amp hour/kg
$BaFeO_4$	257.2	313 Amp hour/kg

The Fe(VI) salt whose preparation is exemplified by, but not limited to either chemical oxidation of Fe(III) or precipitation from another Fe(VI) salt is placed in contact with a conductive material, such as graphite, carbon black or a metal. These and other agents can be formed by mixing with Fe(VI) as a powder, and the powder can be pressed with these and other agents to improve mechanical strength. Rather than mixing with a conductive material, the Fe(VI) salt can be placed in direct contact with a conductive material. These conductive materials include but are not limited to a planar conductive surface, a wire, a porous conductive substrate or a conductive grid.

The anode of the battery may be selected from the known list of metals capable of being oxidized, typical examples being zinc, lithium; common battery anodes such as cadmium, lead and iron; high capacity metals such: aluminum, magnesium, calcium; and other metals such as copper, cobalt, nickel, chromium, gallium, titanium, indium, manganese, silver, cadmium, barium, tungsten, molybdenum, sodium, potassium, rubidium and cesium.

The anode may also be of other typical constituents capable of being oxidized, examples include, but are not limited to hydrogen, (including but not limited to metal hydrides), inorganic salts, and organic compounds including aromatic and non-aromatic compounds.

The electrically neutral ionic conductor utilized in the battery according to the present invention, comprises a medium that can support current density during battery discharge. A typical representative ionic conductor is an aqueous solution preferably containing a high concentration of a hydroxide such as KOH. In other typical embodiments, the electrically neutral ionic conductor comprises common ionic conductor materials used in batteries which include, but are not limited to an aqueous solution, a non-aqueous solution, a conductive polymer, a solid ionic conductor and a molten salt.

In a preferred embodiment of the invention, the cell includes gas separator means such as vent or a void space for preventing the build-up in the cell of oxygen, hydrogen and other gases.

According to another embodiment of the invention, means are provided to impede transfer of chemically reactive species, or prevent electric contract between the anode and Fe(VI) salt cathode. Said means includes; but is not limited to a membrane, a ceramic frit, a non-conductive separator configured with open channels, grids or pores or agar solution; such means being so positioned as to separate said half cells from each other.

An electric storage battery according to the invention may be rechargeable by application of a voltage in excess of the voltage as measured without resistive load, of the discharged or partially discharged cell.

DETAILED DESCRIPTION OF FIGURE 1

Figure 1 illustrates schematically an electrochemical cell 10 based on an Fe(VI) half cell, an electrically neutral ionic conductor and an anode. The cell contains an electrically neutral ionic conductor 22, such as a concentrated aqueous solution of KOH, in contact with an Fe(VI) cathode 14 in form of a pressed pellet containing graphite powder and solid K_2FeO_4. Reduction of Fe(VI) ions such as in the form of FeO_4^{2-} anions, is achieved via electrons available from the electrode 14. The anode electrode 12, such as in the form of metal is also in contact with the electrically neutral ionic conductor 22. Electrons are released in the oxidation of the anode. Optionally, the cell may contain an ion selective membrane 20 as a separator, for minimizing the non-electrochemical interaction between the cathode and the anode.

The invention will be hereafter illustrated by the following Examples, it being understood that the Examples are presented only for a better understanding of the invention without implying any limitation thereof.

Example 1

An experiment was carried out with the object of increasing the half-life of the Fe(VI) chemical species beyond 100 hours, in order to be available for electrochemical reduction.

5   The decomposition rate was characterized using visible absorption spectrum of FeO_4^{2-} in highly alkaline aqueous solution, which exhibits a sharp maximum at 505 nm, an absorption shoulder at 570 nm and two minima at 390 nm and 675 nm. The measured molar absorptivity at 505 nm was 1040 $molar^{-1}$ cm^{-1} and remained constant up to 200 millimolar solutions of

10   K_2FeO_4. The 505 nm absorbance of 2 millimolar K_2FeO_4 was substantially the same in a solution of lithium hydroxide, or up to 15 molar salts of sodium hydroxide or potassium hydroxide.

The electrolytes which were studied for the decomposition rate of FeO_4^{2-} contained various concentrations up to saturation of LiOH, NaOH,

15   KOH and CsOH at 4°C, 22°C and 40°C. The rate of decomposition of FeO_4^{2-} was measured to be directly proportional in first order to the FeO_4^{2-} concentration according to the equation:

$$d[FeO^{2-}] \; / \; dt \; = \; k_f \; [FeO_4^{2-}] \qquad\qquad (3)$$

which yields the half life ($t_{1/2}$) for 50% of the FeO_4^{2-} to decompose, thus

20   resulting:

$$t_{1/2} \; = \; 0.693/k_f \qquad\qquad (4)$$

For this reason, at 22°C in a solution of 5 molar LiOH, FeO_4^{2-} is consumed 50 times faster in a 100 millimolar compared to a solution of 2

25   millimolar FeO_4^{2-} and both solutions have a 34 hours half life expressed as follows:

$$k_f \; = \; 5.7 \; x \; 10^{-6} \; s^{-1} \qquad\qquad (5)$$

The stability of Fe(VI) in other solutions is shown in Table 2.

Table 2

Fe(VI) solubility, S in mM, decomposition rate k_f, and stability time for 0.01 liter
(10 ml) of a molar (M) solution in contact with 0.05 kg (50 g) M_2FeO_4 as predicted
by equation (5)

Solution	Temp	S.mM	K_f, s^{-1}	Fw * (M_2FeO_4)	Stability (days)
5 M LiOH	22°C	940	5.7×10^{-6}	133.8	90
5 M NaOH	22°C	1410	1.8×10^{-5}	165.9	14
5 M KOH	22°C	72	2.4×10^{-5}	198.1	170
5 M C_sOH	22°C	33.7	1.1×10^{-3}	385.6	4
10 M NaOH	22°C	490	1.2×10^{-5}	165.9	55
10 M KOH	22°C	19	6.2×10^{-6}	198.1	240
10 M CsOH	22°C	9.2	6.3×10^{-4}	385.6	26
10 M KOH	40°C	37.5	2.1×10^{-5}	198.1	370
10 M KOH	4°C	8	2.1×10^{-6}	198.1	17,400
15 M NaOH	22°C	146	5×10^{-6}	165.9	480
13 M KOH	22°C	2.9	4.6×10^{-6}	198.1	21,900
Satd. KOH	22°C	1.7	2.1×10^{-7}	198.1	820,000

*Fw – Formula Weight

As can be noticed, in 5 M LioH, NaOH, KOH or CsOH the
decomposition rate increases upon moving down the column of alkali
hydroxides, at 22°C is equal to $t_{1/2}$ being only 10 minutes in the 5 M CsOH
solution. However, at higher hydroxide concentrations, FeO_4^{2-} is more stable
in KOH than in NaOH; thus solutions of 10 M NaOH and KOH electrolytes
have $t_{1/2}$ of 16 and 31 hours respectively, and 15 M NaOH and 13 M KOH
have $t_{1/2}$ of 38 and 42 hours respectively. It was found that the reaction rate k_f
are three fold higher at 40°C and three fold lower at 4°C. At 22°C a saturated

solution of KOH (about 14 molar), the rate of decomposition is lower, k_f being 2.1×10^{-7} s^{-1} with a solution having a half life of 920 hours, more than a hundred fold improvement over the stability in a solution of 5 molar KOH.

The absolute rate of FeO_4^{2-} decomposition is further minimized by
5   several orders of magnitude by determining and utilizing electrolytes which limit its solubility to decrease $d[FeO_4^{2-}]/dt$. To this end, as summarized in Table 2, for NaOH and KOH electrolytes, the solublities of Fe(VI) were measured. At 22°C, in a solution of 5 molar NaOH the solubility of FeO_4^{2-} is over 1.4 moles, while in a saturated solution of KOH it is only 0.0017 molar
10   FeO_4^{2-}. Except for a concentrated (nearly saturated) solution of 5 molar LiOH solution at 22°C, with a millimolar solubility (S) of FeO_4^{2-}, S=940, generally the solubility(s) diminished with an increase of the alkali cation mass. Thus, for a solution of 5 molar NaOH, KOH and CsOH, S was 1410, 72 and 33.7 respectively. In a similar manner, for a solution of KOH of 10
15   molar, 13 molar, and a saturated one, S was 19, 2.9 and 1.7 respectively.

Solubility diminished with a decrease in the temperature and at 60°C, 40°C and 4°C for a saturated KOH solution, S = 4.3, 2.9 and 1.2 respectively. These effects of high alkali cation mass, low temperature and high hydroxide concentration appear to be cumulative, and at 4°C in a solution of 15 moles
20   CsOH, the FeO_4^{2-} is highly insoluble. A further improvement in the FeO_4^{2-} stability is achieved by utilizing an excess of solid Fe(VI) in contact with a low solubility of Fe(VI) solution. Extended results over several weeks on the solution decomposition are shown in Figure 2. Thus, in a saturated solution of KOH containing an excess of solid KOH, a solution with an initial
25   concentration of 1.7 millimolar of K_2FeO_4 lost only 0.3 millimolar of active Fe(VI) in 100 hours. In a second experiment a six fold excess, of the K_2FeO_4, beyond the saturation point was added to a saturated solution of KOH. As shown in Figure 2, after one month the solution contains a constant concentration of dissolved FeO_4^{2-}. These results provide a pathway to

prepare stable concentrations of Fe(VI). This is represented schematically in the inset of Figure 2. The electrolyte is based on a concentrated hydroxide solution, containing a cation which inhibits decomposition, such as K^+. The solution is saturated not only with K_2FeO_4, but also contains an excess of

5   solid K_2FeO_4. The generalized system utilizes mass (m) of Fe(VI) salt with formula weight (FW) in contact with a volume of a solution (V). The dissolution of said mass, provides a constant saturated concentration (S) of Fe(VI). The required stable time (t_{stable}) which is necessary for Fe(VI) concentration to be below S is represented by the formula:

10            $$t_{stable} = m \ FW^{-1} \ V^{-1} \ k_f^{-1} \ s^{-1} \qquad\qquad (5)$$

Using the measured values of S and k_f, Table 2 presents the predicted life-time of a system containing 0.05 kg (50 g) of M_2FeO_4 in contact with 0.01 liter (10 ml) of the respective alkali hydroxide. A saturated KOH is an attractive electrolyte, minimizing both the solubility and the rate of loss of

15   K_2FeO_4. When decomposition occurs, the excess of solid K_2FeO_4 dissolves providing a constant buffer source to maintain a corresponding saturated solution with a predicted life-time of the K_2FeO_4 of over 1,000 years.

Release of the cathode materials into the environment would result in a dilution of the hydroxide, which will enhance the FeO_4^{2-} dissolution and a

20   rapid degradation to an innocuous FeOOH according to equation (1).

Example 2

An experiment was carried out in order to determine the capability of achieving a high voltage and the theoretical three electron reduction capability in discharge of Fe(VI) salts in solutions as expressed in the equation. This

25   was examined by a galvanostatic reduction of dissolved Fe(VI) in a 13.5 molar solution of potassium hydroxide.

Figure 3, shows the time evolution of the potential, during Fe(VI) reduction. In an initial concentration $c_{initial}$ = 2.5 millimolar of K_2FeO_4, in

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volume V = 0.5 ml of a solution of 13.5 molar KOH was reduced at a current density J = 0.100 mA/cm^2, and a subsequent continued reduction at J=0.010 mA/cm^2, on a Pt electrode with a surface area, A = 10 cm^2. Integration of the charge transferred, q = t J A/F (F being the Faraday constant and t being time)

5   yields the relative oxidation state = q / (Vcinitial) compared to the charge of the Fe(III) product. As shown in Figure 3, the solid curve 1 illustrates the oxidation state of the starting material which approaches Fe(VI) according to the equation and yields the +6 valence state of iron. After completion of the three electron transfer, the negative shift in the potential as illustrated in

10   Figure 3 is consistent with the depletion of the initial Fe(VI) and subsequent hydrogen evolution. A cathode half cell with a more positive redox couple will result in a higher voltage battery, and the Fe(VI) half cell has a high positive redox potential. Terminating the discharge in Figure 3 after 1, of the 3 electrons per Iron, has been transferred forms a solution containing on the

15   average Fe(V), for example as in the form of FeO$_4^-$. Stopping the discharge in Figure 3 after 2, of the 3 electrons per Iron, has been transferred forms a solution containing on the average Fe(IV), for example as in the form of FeO$_3^{2-}$. Respectively, in these latter two cases, recommencing the reduction results in discharging a Fe(V) or a Fe(VI) battery.

20   The measured redox potentials at a platinum electrode, of 2 milimolar, 20 milimolar, 60 milimolar and 100 millimolar of K$_2$FeO$_4$ in various solutions of sodium hydroxide show that they are positive, increase with Fe(VI) concentration and decrease with the hydroxide concentration.

          Generally, this redox potential varied from E(15 molar NaOH, 2

25   milimolar K$_2$FeO$_4$) = 0.5 V to E(5 molar NaOH, 100 milimolar K$_2$FeO$_4$) = 0.7 V, measured in volts versus the standard hydrogen electrode, and were similar values in solutions of KOH.

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Example 3

As summarized in Table 3, the observed steady state current densities at 22° are low, less than 100 $\mu A/cm^2$ for reduction of 2mM (millimolar FeO_4^{2-}). This may be improved six fold by use of a high surface area porous Ni substrate, although the resultant current density of 0.4 mA/cm^2 remains too low for many battery applications. These current densities are dramatically improved through formation of a solid K_2FeO_4 pellet, containing 30% by weight of micro particulate graphite (2 μm powder) to improve conductivity. A hundred fold increase in current occurs, as observed in Table 3, in comparison of the planar electrocatalysts to the solid K_2FeO_4 /μcarbon electrode; with current densities of 10 mA/cm^2 and higher are sustained. The solid K_2FeO_4 pellet capacity and voltage are low without added graphite, and improves at lower current density, J. As shown in Table 3, the addition of up to 10% graphite, by weight, further improves both capacity and voltage of the redution of Fe(VI) cathode during discharge.

<u>Table 3</u>

<u>Maximum steady state cathodic current density and polarization losses for</u>
<u>Fe(VI) reduction at various electrodes and various solutions at 22°C. Fe(VI)</u>
<u>refers to K_2FeO_4 ; C refers to graphite.</u>

Electrode	Solution	Polarization losses MV cm^2 mA^{-1}	Maximum Current mA cm^{-2}
	2mM Fe(VI)		
Flat Ni	13.5M KOH	700	0.07
	2mM Fe(VI)		
Flat Pt	13.5M KOH	500	0.06

|			
Porous Ni 60 pores/inch	2mM Fe(VI) 13.5M KOH	150	0.4
100% Fe(VI) in 50 mg disc	13.5M KOH	120	0.5
95% Fe(VI), 5%C in 50 mg disc	13.5M KOH	60	2
90% Fe(VI), 10%C in 50 mg disc	13.5M KOH	30	5
70 % Fe(VI), 30%C in 50 mg disc	13.5M KOH	20	10
70% Fe(VI), 30%C in 50 mg disc	10M KOH	15	20

Example 4

This example illustrates the use of zinc metal anodes, and that during discharge with these anodes a high fraction of the electrical storage capacity of such super iron Fe(VI) salts as K_2FeO_4 (with 406 Ah/kg storage capacity, Table 1), and other salts listed in Table 1 such as S_rFeO_4, Ag_2FeO_4, $CaFeO_4$ and $BaFeO_4$, is achieved.

The super iron cathode may be combined with a zinc anode to form a super iron/zinc battery. In alkaline solutions, the oxidation of zinc is:

- 14 -

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \tag{6}$$
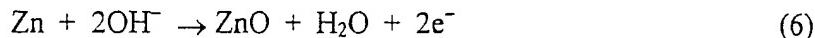
Combined with equation 2, this describes a discharge of the super iron-zinc battery, as follows:

$$2FeO_4^{2-} + 3\ Zn + 3H_2O \rightarrow 3ZnO + 2FeOOH + 4OH^- \tag{7}$$
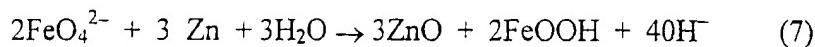
5   The super iron-zinc batteries, for example as based on the Fe(VI) salt K_2FeO_4, have a theoretical specific energy higher than conventional aqueous (alkaline, metal hydride, lead or Ni/Cd) batteries, of:

$$1.8\ \text{Volt} \times 271\ \text{Ah/kg} = 490\ \text{Wh/kg.} \tag{8}$$

     Super iron/zinc batteries, consisting of planar zinc and solid $K2FeO_4$

10 salt/μcarbon electrodes separated by 10 or 13.5 M KOH were discharged at 22°C. The battery had a measured open circuit voltage of 1.7 to 1.8 V. Excess zinc was utilized to produce a FeO_4^{2-} limited capacity cell, and determine the coulombic efficiency of the three electron reduction, eq 2. This efficiency is experimentally determined by comparing the coulombs generated

15 during discharge to the theoretical faradaic equivalents available in the mass of K_2FeO_4, SrFeO, Ag_2FeO_4, $CaFeO_4$ or $BaFeO_4$. As seen in Figure 4, at low current density discharge of 0.6 mA/cm^2, over 85% of the theoretical 3 e^- per FeO_4^{2-} is attained. Over 65% efficiency is measured at 3.5 mA/cm^2. Similar discharges are measured when the electrodes are separated by 10M KOH.

20 Cells also discharge well with small volumes of aqueous solution. As illustrated in Figure 4, the Ag_2FeO_4/Zinc battery exhibits a second lower voltage plateau leading to extended discharge behavior. Without being bound to any theory, this is related to the discharge of both Fe(VI) and Ag(I) according to:

25      $$Ag_2FeO_4 + 3H_2O + 5e^- \rightarrow FeOOH + 2Ag + 5OH^- \tag{9}$$
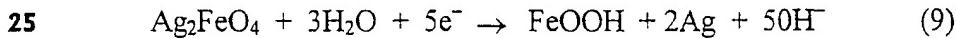
     A measured comparison of a super iron/zinc battery compared to a conventional alkaline battery is illustrated in Figure 5. Hence, a conventional alkaline button configuration cell was discharged under a constant 3000 ohm

load, and the specific energy determined as the cell potential multiplied by the current over time and divided by the mass. The 0.399g mass of the cell was composed of 0.139g Zn, electrolyte and separator, as well as 0.260g of MnO_2 containing cathode. In the super iron/zinc battery a second conventional cell is opened and the MnO_2 containing cathode is replaced by 0.180g of Fe(VI) cathode comprised by mass of 90% K_2FeO_4 and 10% graphite. As illustrated in Figure 5, under the same 3000 ohm discharge charge load, the super iron cell delivers a storage capacity of approximately 250 W/kg, over a 160% increase compared to that in the conventional alkaline battery.

Example 5

This example illustrates the use of cadmium metal anodes, with the Fe(VI) half-cell cathode and rechargeability of a super iron battery. Super iron/cadmium batteries, consisting of planar cadmium and solid K_2FeO_4/μcarbon electrodes separated by 13.5 M KOH were discharged at 22°C. The battery had a measured open circuit voltage of 1.3 V, and the discharge at constant current is used to measure the storage capacity where the current, i, multiplied by the time and divided by the mass of the K_2FeO_4, provides the measured K_2FeO_4 storage capacity = i t / mass K_2FeO_4. As seen in Table 4, at low current density discharge of 0.4 mA/cm, a high storage capacity of 390 Amp hour/kg is attained. A 219 Amp hour/kg storage capacity is measured at 4 mA/cm^2. Table 4 includes repeated 1 mA/cm^2 discharge of super iron/cadmium batteries during three charge/discharge cycles. Partial reduction of Fe(VI) salts may cause, in addition to Fe(III) salts, formation of Fe(V) and Fe(IV) salts. Albeit at a lower capacity than the Fe(VI) half cell battery, these Fe(V) and Fe(IV) salts can be used as super iron half cells to also provide a high capacity super iron battery.

Table 4

Discharge and charge/discharge of a cell containing a 1 cm^2 50mg K$_2$FeO$_4$

(as 70%. 30% 2μm graphite) cathode and a cadmium anode in 13.5 M KOH

5   at 22°C. Each cycle 1 is prior to any recharge. Cycles 2 and 3 are subsequent

to 5 mA/cm^2 recharge

Cycle 1	Discharge Current	Measured K$_2$FeO$_4$ Storage Capacity
1	0.4 mA	390 Amp hour/kg
1	1.0 mA	329 Amp hour/kg
1	1.0 mA	329 Amp hour/kg
2	1.0 mA	207 Amp hour/kg
3	1.0 mA	195 Amp hour/kg
1	4.0 mA	219 Amp hour/kg

CLAIMS:

1.   A storage battery, comprising two half-cells which are in electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises a cathode in form of a solid-phase Fe(VI) salt in an amount of at least 1% of the half-cell weight, whereby electrical storage is accomplished via electrochemical reduction to a valence of iron salt less than Fe(VI).

2.   The battery according to Claim 1, wherein said Fe(VI) salt includes a cation, selected from the group consisting of the alkali metal cations, ammonium H^+ alkali earth metal cations, transition metal cations, and cations of groups III, IV and V of the periodic table.

3.   The battery according to Claim 1 or 2, wherein said anode includes a metal capable of being oxidized.

4.   The battery according to Claim 3, wherein said metal is selected from the group consisting of zinc, lithium, magnesium, calcium, aluminium, cadmium, lead, iron, copper, cobalt, nickel, chromium, titanium, gallium, indium, manganese, silver, cadmium, barium tungsten, molybdenum, sodium, potassium, rubidium and cesium.

5.   The battery according to Claim 1 or 2, wherein said anode includes hydrogen capable of being oxidized.

6.   The battery according to Claim 1 or 2, wherein said anode includes an inorganic salt capable of being oxidized.

7.   The battery according to Claim 1 or 2, wherein said anode includes an organic compound capable of being oxidized, selected from the group consisting of aromatic and non-aromatic compounds.

8.   The battery according to Claim 1 or 2, wherein said electrically neutral ionic conductor is an aqueous solution.

9. The battery according to Claim 1 or 2, wherein said electrically neutral ionic conductor is a non-aqueous solution.

10. The battery according to Claim 1 or 2, wherein said electrically neutral ionic conductor is a conductive polymer.

11. The battery according to Claim 1 or 2, wherein said electrically neutral ionic conductor is a molten salt.

12. The battery according to Claim 1 or 2, wherein said electrically neutral ionic conductor is a solid ionic conductor.

13. The battery according to Claim 8, wherein said solution contains hydroxide ions.

14. The battery according to Claim 8, wherein said solution contains dissolved $Fe(VI)$ salt.

15. The battery according to Claim 1 or 2, further characterized in that said $Fe(VI)$ salt is in contact with a conductive material.

16. The battery according to Claim 15, wherein said conductive material is selected from the group of graphite, carbon black and metals.

17. The battery according to Claim 15, wherein conductive material comprises a mixed pressed powder.

18. The battery according to Claim 15, wherein said conductive material comprises a planar surface or a wire.

19. The battery according to Claim 15, wherein said conductive material comprises a porous substrate or grid.

20. The battery according to Claim 1 or 2 further comprising means to impede transfer of chemically reactive species between said two half-cells.

21. The battery according to Claim 20, wherein said means is a non conductive separator configured with open channels, grids or pores.

22. The battery according to Claim 1 or 2, wherein said electrically neutral ionic conductor contains a further solid solute or dissolved liquid for improving the stability of $Fe(VI)$ and effectiveness of cell discharge.

23. The battery according to Claim 22, wherein said further solid solute is selected from KOH and CsOH.

24. The battery according to Claim 22, wherein said further solid solute is selected from LiOH and NaOH.

25. The battery according to Claim 22, wherein said further dissolved liquid is an aqueous solution.

26. The battery of Claim 20 in which said means to impede chemically reactive ion transfer comprises a membrane positioned to separate said half cells.

27. The battery according to Claim 22, wherein said further dissolved liquid is a non-aqueous solution.

28. The battery according to Claim 1 or 2, wherein said cell is rechargeable by application of a voltage in excess of the discharge cell open circuit potential.

29. The battery of Claim 8, wherein said solution contains the concentration of up to 5 molar hydroxide ions.

30. The battery of Claim 8, wherein said solution contains the concentration from 5 to 10 molar hydroxide ions.

31. The battery of Claim 8, wherein said solution contains the concentration from 10 molar to a solution saturated in hydroxide ions.

32. The battery according to Claim 13, wherein the concentration of said Fe(VI) salt is at least 0.0001 molar.

33. The battery of Claim 8, wherein the concentration of said Fe(VI) salt is above 0.0001 molar.

34. The battery of Claim 8, wherein the concentration of said Fe(VI) ions is above 0.01 molar.

35. The battery of Claim 8, wherein the concentration of said Fe(VI) ions is at or above 1 molar.

36. The battery according to Claim 1 or 2 including a gas separator means for preventing the build-up of oxygen, hydrogen and other gases.

37. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises at least 1% of weight as an Fe(V) salt, wherein the discharge in the electrical storage cell is based on the reduction of the Fe(V) salt.

38. A battery comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises an anode and the other half-cell comprises at least 1% of weight as an Fe(IV) salt, wherein the discharge in the electrical storage cell is based on the reduction of the Fe(IV) salt.

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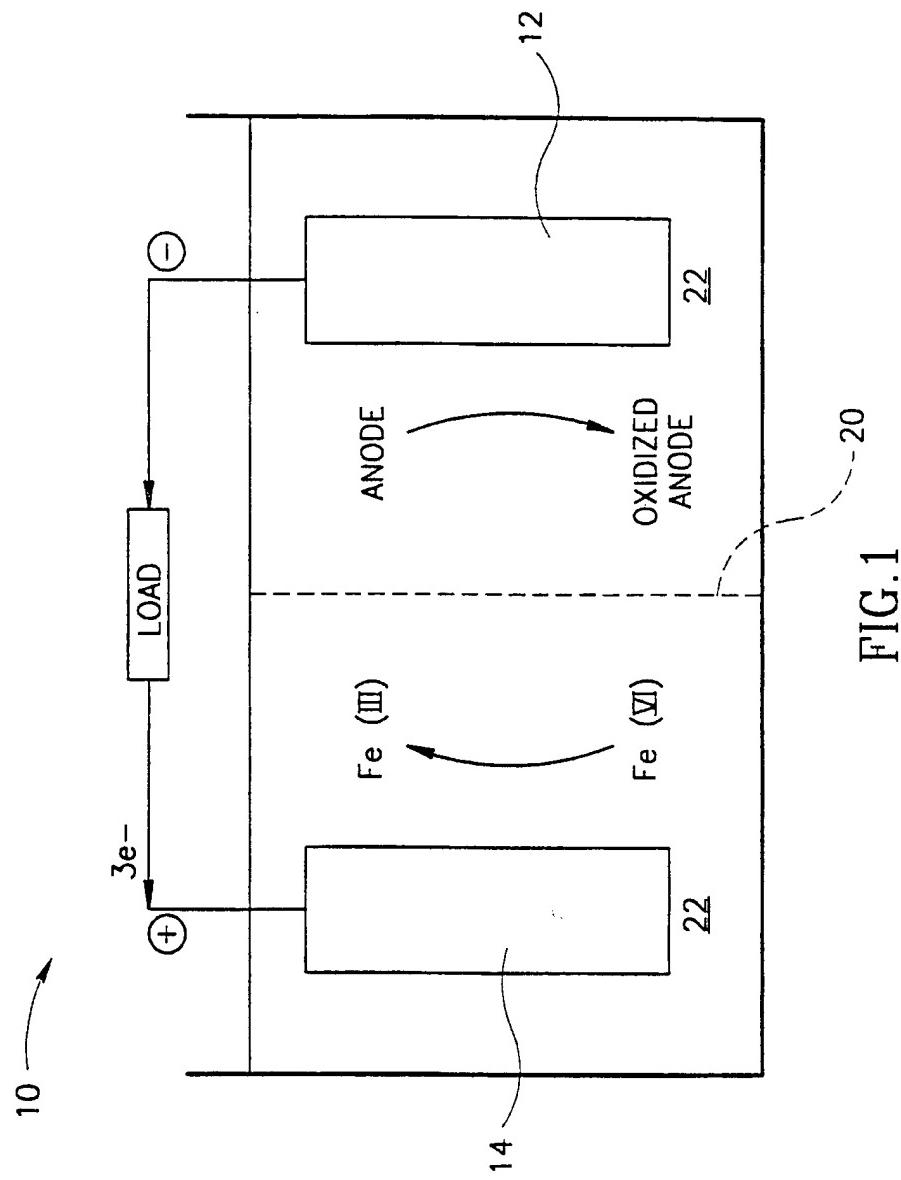
FIG.1

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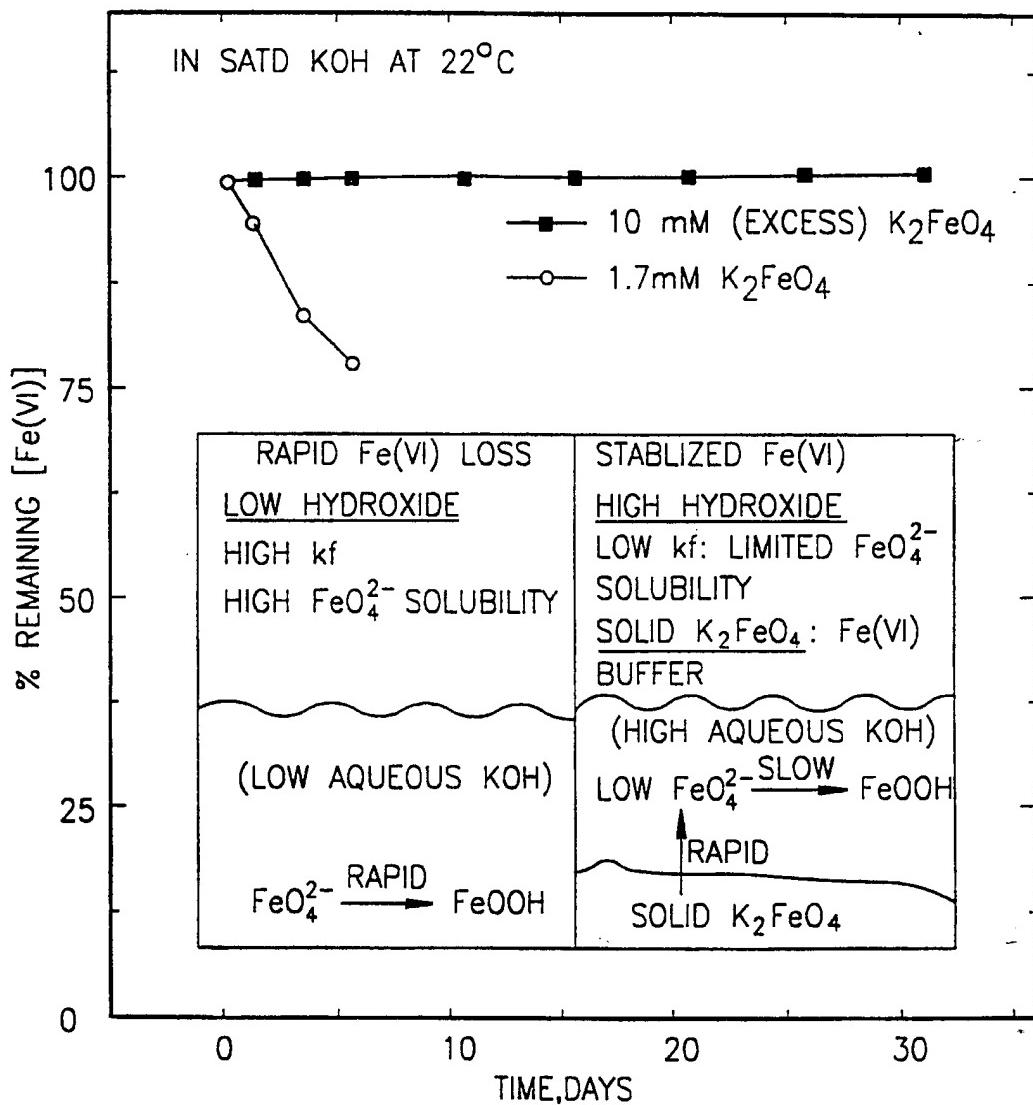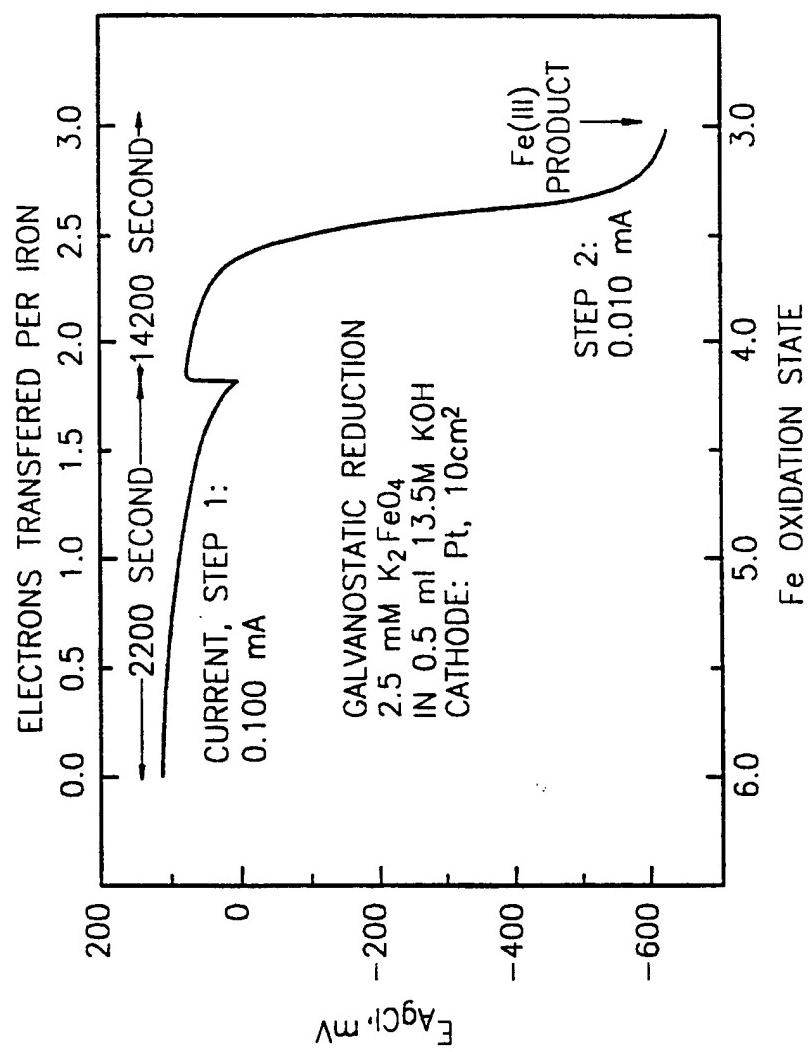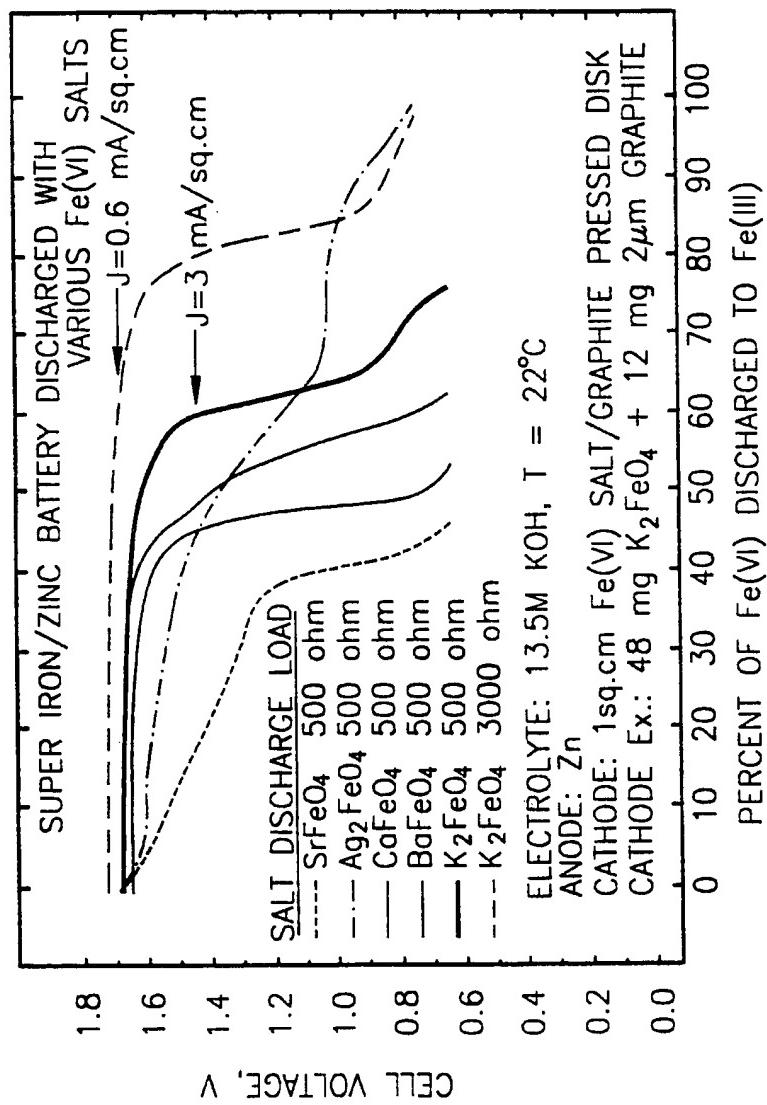
IN SATD KOH AT 22°C

Legend:
- ■ 10 mM (EXCESS) K_2FeO_4
- ○ 1.7mM K_2FeO_4

Y-axis: % REMAINING [Fe(VI)]

X-axis: TIME, DAYS

Inset box (left):
RAPID Fe(VI) LOSS
LOW HYDROXIDE
HIGH kf
HIGH FeO_4^{2-} SOLUBILITY

(LOW AQUEOUS KOH)

$FeO_4^{2-} \xrightarrow{RAPID} FeOOH$

Inset box (right):
STABLIZED Fe(VI)
HIGH HYDROXIDE
LOW kf: LIMITED FeO_4^{2-} SOLUBILITY
SOLID K_2FeO_4: Fe(VI) BUFFER

(HIGH AQUEOUS KOH)
LOW $FeO_4^{2-} \xrightarrow{SLOW} FeOOH$
↑ RAPID
SOLID K_2FeO_4

FIG.2

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FIG.3

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FIG.4
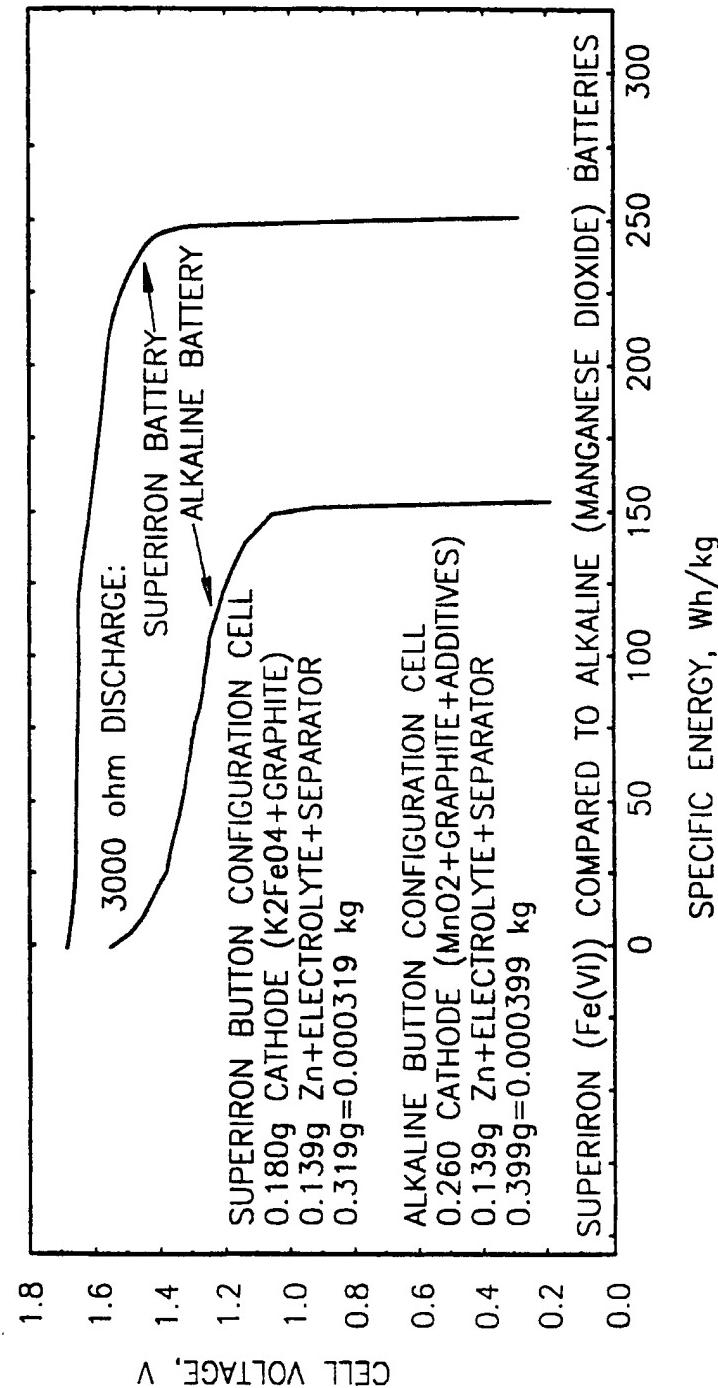
FIG.5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   H01M4/52   H01M4/58   H01M4/36   H01M8/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 675 256 A (WINCHESTER CLINTON S ET AL) 23 June 1987 see claims 1-5; example 1 ---	38
X	US 4 567 031 A (RILEY BRIAN) 28 January 1986 see column 1, line 5 - line 10; claim 1 ---	38
A	EP 0 012 943 A (GIPELEC) 9 July 1980 see claims 1-6 ---	1-38
A	US 4 795 685 A (BONES ROGER J ET AL) 3 January 1989 see claims 1-9 ---	1-38
A	US 4 451 338 A (DEININGER J PAUL ET AL) 29 May 1984 see claims 1-41 -----	1-38

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
26 August 1998	02/09/1998

Name and mailing address of the ISA	Authorized officer
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